9th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 18–22, 2001

Homogeneous broadening of the zero optical phonon spectral line in semiconductor quantum dots

S. V. Goupalov†‡, R. A. Suris† and P. Lavallard§
† Ioffe Physico-Technical Institute, St Petersburg, Russia
‡ Department of Physics, Washington State University,
Pullman, Washington 99164-2814 USA
§ Groupe de Physique des Solides, Universités Paris 6 et 7, 75251 Paris, France

Introduction

In recent years semiconductor quantum dots (QDs) have been attracting much attention due to their promising advantages in optoelectronic device applications. Investigation of different mechanisms leading to homogeneous broadening of optical spectral lines in QDs, stimulated by experimental studies [1], is therefore of utmost importance. Various theoretical treatments applicable to this problem were developed more than 30 years ago for multi-phonon-assisted optical transitions of electrons localized on lattice defects (for a review see [2] and Refs. therein). In the adiabatic approximation the crystal nuclear system is treated as the slowest one. The relatively fast motion of the electron localized on a lattice defect or exciton localized in a QD is perturbed by the electron-phonon interaction which is supposed to be linear in the nuclear displacement. The perturbed energy of the localized electron (exciton) serves as an adiabatic potential for the nuclear system. The perturbation is usually considered up to the second order. As a result, parabolic adiabatic potentials for the nuclear motion corresponding to the crystal ground state and to a state, where the localized electron or exciton is excited, differ. The first-order perturbation term leads to a difference in the parabolic potentials minima positions while the second-order term leads to a difference in their frequencies. As a result, the phonon wave functions of the ground and the excited states are no longer orthogonal and multi-phonon-assisted transitions become possible.

In case of optical phonons possessing relatively high frequency several spectral lines corresponding to phonon-assisted transitions are usually experimentally resolved. In what follows we will be interested in the zero optical phonon line (ZOPL) broadening. As it was pointed out by Krivoglaz [3], the first-order perturbation term can not lead to the zero-phonon line broadening unless the phonon damping is taken into account. At the same time, the second-order term does lead to the finite zero-phonon line width [3].

On the other hand, due to a strong interaction of electrons with acoustic phonons in a QD, the latter should contribute substantially to the ZOPL width [4, 5]. Since the frequencies of acoustic phonons are much less than that of optical ones, the ZOPL broadening may be caused by multiple acoustic phonon assisted transitions governed by the first order perturbation term.

The aim of this work is to calculate the contributions to the ZOPL homogeneous broadening due to both optical and acoustic phonons making the most reasonable assumptions and to compare them for a one particular QD system. Since the available experimental data [1] were obtained for CdSe spherical nanocrystals of the radius R less than the exciton Bohr radius in a bulk material, we have chosen this system for our study.

1. Homogeneous broadening due to optical phonons

Let us consider the homogeneous broadening of the ZOPL associated with an optical transition to the ground ($1S_e1S_{h,3/2}$) state of the exciton confined in a spherical CdSe nanocrystal. In this section we will discuss the broadening governed by the second-order perturbation term [7] $\sum_{æ} B_{æ,s}\hat{a}_{æ}^{+}\hat{a}_{æ}$, where $\hat{a}_{æ}^{+}$ and $\hat{a}_{æ}$ are the phonon creation and annihilation operators,

$$B_{æ,s} = \sum_{s' \neq s} \frac{\left| V_{ss'}^{æ,e} + V_{ss'}^{æ,h} \right|^2}{E_s^0 - E_{s'}^0}, \tag{1}$$

$s = 1S_e1S_{h,3/2}$, the subscript s' enumerates the upper exciton states, the index æ enumerates different phonon modes, $V_{ss'}^{æ,e}\left(V_{ss'}^{æ,h}\right)$ is the matrix element of electron(hole)-phonon interaction, E_s^0 is the exciton energy in the state s. Here we will consider the Fröhlich polar electron-phonon interaction and treat optical phonons as in Ref. [8]. In this treatment the quantized polar phonon modes, characterized by the phonon total angular momentum $\mathcal{F}$, have, generally speaking, a mixed LO-TO character. However, in what follows we will consider only modes with $\mathcal{F} = 0$ which are purely longitudinal. The boundary condition of the relative sublattice displacement vanishing at the nanocrystal surface is also supposed to be applicable. Thus, the electrostatic potential induced by the polar optical phonon modes with the total angular momentum $\mathcal{F} = 0$ is given by $\Phi(x, R) = \sum_{æ} \phi_{æ}(x, R)\left(\hat{a}_{æ}^{+} + \hat{a}_{æ}\right)$, where the sum is hold over the phonon modes with $\mathcal{F} = 0$,

$$\phi_{æ}(x, R) = \sqrt{\frac{\hbar}{\omega_{æ}}(\varepsilon_0 - \varepsilon_\infty)}\frac{\omega_{TO}}{\varepsilon_\infty \nu_{æ}\sqrt{R}}\,\frac{j_0(\nu_{æ}) - j_0(\nu_{æ}x)}{|j_0(\nu_{æ})|}, \tag{2}$$

$x = r/R$, $j_l(x)$ is the spherical Bessel function of the l-th order, ε_0 and ε_∞ are the CdSe static and high-frequency dielectric constants, respectively, $\nu_{æ} = \sqrt{\omega_{LO}^2 - \omega_{æ}^2}R/\beta_L$, $\omega_{LO}(\omega_{TO})$ is the bulk LO(TO)-phonon frequency, β_L is the LO-phonon dispersion parameter, the phonon mode frequencies are defined by equation $j_1(\nu_{æ}) = 0$. The lowest exciton state which mainly contributes to the sum in the right-hand part of Eq. (1) is the state $\tilde{s} = 1S_e2S_{h,3/2}$. The matrix element of the exciton-phonon interaction between this state and the exciton ground state is given by

$$V_{s\tilde{s}}^{æ,e} + V_{s\tilde{s}}^{æ,h} = e\int_0^1 dx\left\{-2\sin^2\pi x + x^2\left[f_0^s(x)f_0^{\tilde{s}}(x) + f_2^s(x)f_2^{\tilde{s}}(x)\right]\right\}\phi_{æ}(x, R), \tag{3}$$

where e is the electron charge, $f_0^s(x)$, $f_2^s(x)$ are dimensionless functions defined in Ref. [7] and describing the radial dependence of the hole envelope wave function. If we neglect phonon damping and omit in the adiabatic phonon Hamiltonians contributions arising from the first-order perturbation term, then we will find that the cross-section of light absorption by the QD is proportional to [3]

$$\sigma_a(\Omega) \propto \exp\left[-\frac{(\Omega - \Omega_{fi})^2}{2\delta_{opt}^2}\right], \quad \delta_{opt}^2 = \sum_{æ} \bar{n}_{æ}(\bar{n}_{æ} + 1)B_{æ}^2, \tag{4}$$

where Ω is the light frequency, $\hbar\Omega_{fi}$ is the energy difference of the electron system before and after the optical transition, $\bar{n}_{æ} = (\exp\beta_{æ} - 1)^{-1}$, $\beta_{æ} = \hbar\omega_{æ}/T$, T is the temperature in energy units. Thus, for high temperatures $\delta_{opt} \propto T$ while at $T \to 0$ it vanishes very rapidly as $\exp(-\beta_{æ}/2)$. Since the energy of confined exciton $E_s^0 \propto R^{-2}$, from Eqs. (1)–(4) it follows that $\delta_{opt} \propto R$.

2. Homogeneous broadening due to acoustic phonons

In this section we will discuss the broadening of the ZOPL due to the first order perturbation term $\sum_{æ} A_{æ}\left(\hat{a}_{æ}^{+} + \hat{a}_{æ}\right)$. In the strong coupling approximation one obtains [4, 5]

$$\sigma_a(\Omega) \propto \exp\left[-\frac{(\Omega - \Omega_{fi} + \Delta_{ac})^2}{2\delta_{ac}^2}\right], \quad \delta_{ac}^2 = \sum_{æ} \frac{A_{æ}^2}{\hbar^2} \coth\frac{\beta_{æ}}{2}, \tag{5}$$

where $\Delta_{ac} = \sum_{æ} A_{æ}^2/\hbar^2\omega_{æ}$. For high temperatures $\delta_{\mathrm{ac}} \propto \sqrt{T}$ while for $T \to 0$ it tends to a constant value.

Here we will treat acoustic phonons as in Ref. [7], where it was shown that the spectrum of the acoustic vibration modes of a semiconductor QD embedded in a glass matrix is continuous and contains maxima corresponding to the acoustic phonon resonant reflection from the QD surface. We will again restrict our consideration to the case of $\mathcal{F} = 0$ vibrational modes, which in fact play the major role in the ZOPL broadening, and treat the exciton-phonon interaction in the framework of the deformation potential approximation. Thus we obtain

$$\delta_{ac}^2 = \frac{\hbar}{4\pi^2\rho_{out}R^4c_l^{(in)}} \int_0^{\infty} dy\, y^3 \coth\left(\frac{\hbar c_l^{(in)} y}{2RT}\right) \left(\frac{c_l^{(out)}}{c_l^{(in)}}\right)^4 \frac{y^4}{Y^2(y)} F^2(y), \tag{6}$$

where $c_l^{(\mathrm{in})}\left(c_l^{(\mathrm{out})}\right)$ is the longitudinal sound velocity inside (outside) the QD, $\rho_{\mathrm{in}}(\rho_{\mathrm{out}})$ is the mass density inside (outside) the QD, $Y(y)$ is the function given in an explicit form in Ref. [7] and dependent on $c_l^{(\mathrm{in})}$, $c_l^{(\mathrm{out})}$, ρ_{in}, ρ_{out} and the transversal sound velocities inside and outside the QD,

$$F(y) \approx \int_0^1 dx \left\{a_v x^2\left[f_0^{s\,2}(x) + f_2^{s\,2}(x)\right] + 2a_c \sin^2\pi x\right\} j_0(xy),$$

a_c, a_v are the deformation potential constants defined as in Ref. [7].

3. Results and discussion

The calculated QD size dependencies of δ_{ac} and δ_{opt} for $T = 300K$ are shown in Fig. 1(a). For small QD radii the contribution to the ZOPL homogeneous broadening due to acoustic phonons predominates. As QD radius increases, the role of optical phonons in the ZOPL broadening increases and their contribution to the ZOPL width can exceed that of acoustic phonons. For higher temperatures the role of optical phonons becomes more important while for lower temperatures the ZOPL broadening is mainly governed by acoustic phonons. The temperature dependence of their contribution is shown in Fig. 1(b) for a 11 Å-size

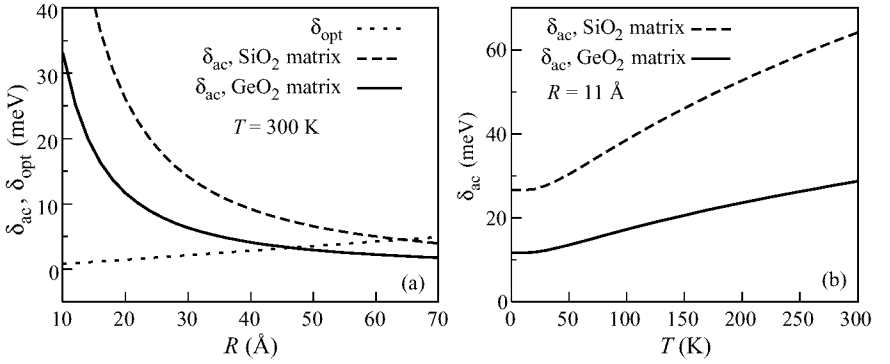

Fig. 1. (a): Dependencies of δ_{opt} (dotted line) and δ_{ac} (solid and dashed lines) on CdSe QD radius for $T = 300K$. Solid and dashed lines correspond to the GeO_2 and SiO_2 host matrices, respectively. (b): Temperature dependencies of δ_{ac} for a 11 Å-size CdSe QD embedded in a GeO_2 (solid line) and SiO_2 (dashed line) matrix.

QD embedded in different glass matrices and is in a good agreement with the ZOPL homogeneous linewidth temperature dependence obtained from experimental studies [ ]. One can see from Fig. 1(a,b) that the ZOPL homogeneous broadening due to acoustic phonons is strongly dependent on the elastic properties of the host matrices.

Acknowledgements

We are grateful to D.S. Citrin for useful discussions. Support of INTAS (code 99-O-0858) is gratefully acknowledged. The work of SVG was supported in part by the Office of Naval Research and the National Science Foundation through ECS-0072986, DMR9705403, and DMR-0073364.

References

[1] R. W. Schoenlein *et al.*, *Phys. Rev. Lett.* **70**, 1014 (1993).
[2] Yu. E. Perlin, *Usp. Fiz. Nauk* **80**, 553 (1963).
[3] M. A. Krivoglaz, *Fiz. Tverd. Tela* **6**, 1707 (1964).
[4] T. Takagahara, J. Lumin. **70**, 129 (1996).
[5] X.-Q. Li and Y. Arakawa, *Phys. Rev. B* **60**, 1915 (1999).
[6] E. Roca, C. Trallero-Giner and M. Cardona, *Phys. Rev. B* **49**, 13704 (1994).
[7] S.V. Goupalov and I.A. Merkulov, Fiz. Tverd. Tela **41**, 1473 (1999).